RASHED TALEB RASHEED, TATJÁNA JUZSAKOVA, ENDRE DOMOKOS, ALI DAWOOD SALMAN, AL-LAMI MUNAF	WATER USING MNO2 NANOPARTICLES MODIFIED MWCNTS		14:10
LUNCH BREAK			**14:10-15:10**
COFFEE BREAK AT FACULTY HALL			15:20-15:30
Session 6	**Session Chairs**	Presentation	Time
15:30 – 16:50	**Rita Bodáné-Kendrovics - Visnja Mihajlovic**		
ROQUIA I. RIZK, TATJANA JUZSAKOVA, ENDRE DOMOKOS, RAWASH MOHAMED ALI	BIO REMOVAL OF HEAVY METAL BY USING OF WATER HYACINTH PLANTS	(ORAL)	15:30-15:40
OYA AYDIN URUCU, ASLI BEYLER ÇİĞİL, EMINE ARMAN KANDIRMAZ	COLORIMETRIC DETERMINATION OF VANADIUM IN WATER SAMPLES	(ORAL)	15:40-15:50
LARBI EDDAIF, ABDUL SHABAN, JUDIT TELEGDI	CALIX[4]RESORCINARENE AND CALIX[4]ARENE IONOPHORES: A HEAVY METALS IONS DETECTION APPLICATION	(ORAL)	15:50-16:00
BALÁZS GYULA URBÁN, CSABA MÁTÉ KASSAI, NÁNDOR MÉSZÁROS	BLURRED TIRE TRACKS QUANTITATIVE DATA ON MICROPARTICLES FROM TIRE WEAR ON ROAD SURFACE WASHING INTO SURFACE WATER	(ORAL)	16:00-16:10
MUNGUNZAYA GANBAT, KATALIN KOVÁCS, JUDIT PLUTZER, HOSAM BAYOUMI HAMUDA	EVALUATION OF THE POSSIBLE ADVERSE EFFECT OF WASTEWATER DISCHARGES WITH ACUTE TOXICITY TESTS	(ORAL)	16:10-16:20
VERA MALSIA LUSHAJ, BASHKIM LUSHAJ	MODULE ON SOCIO-ENVIRONMENTAL IMPACT ASSESSMENT (EIA) IN ECO-	(ORAL)	16:20-16:30

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CALIX[4]RESORCINARENE IONOPHORES: A HEAVY METALS IONS DETECTION APPLICATION

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Abstract:

*The present investigation is centered on the use of macrocycles as sensing platforms for the heavy metals ions (HM) monitoring and detection. Primarily, novel calix[4]resorcinarenes were successfully synthesized, namely: C-dec-9-enylcalix[4]resorcinarene-O-(S-)-a-methylbenzylamine (**Compound B**) and C-dec-9-enylcalix[4]resorcinarene-O-(R+)-a-methylbenzylamine(**Compound C**). Their detailed chemical and structural characterization was carried out by means of ^{1}H NMR/ ^{13}C NMR, and FTIR. Other properties (Crystallinity degree and thermal behavior) were examined by P-XRD and TG-DSC-MS. In addition, the macrocycles were deposited onto gold surfaces of quartz crystal resonators in nanolayers to produce functioning detection and QCM-I based ion-selective electrodes. The results were interesting, and showing the detection ability of different HM (Only Pb^{2+} ions are discussed here) in aqueous solution, in low concentrations (ppm level). The calix-QCM based chemosensors showed noble linear ranges and sensitivities. Furthermore, the detection limits were 0.45 and 0.30 ppm for compounds B and C respectively.*

Keywords:
Chemosensors, calix[4]resorcinarenes, heavy metal ions, detection, QCM-I.

1. INTRODUCTION

The heavy metals ions (HM) are chemicals found either naturally or artificially (industrial activities…etc.), and are posing great harms to the human health (various cancers, Alzheimer…etc.), as well to the environment (soil and water pollutions) [1]. Their detection is a goal of particular importance, they're mainly monitored by highly sensitive and selective analytical techniques, such as Inductively Coupled Plasma (ICP), Atomic Absorption Spectroscopy (AAS), Neutral Activation (NA)…etc. Unfortunately, the previously mentioned procedures require professional skills, sample preparation and preconcentration procedures, other factors such as high cost and time consumption are making their use restricted. As an alternative, the 'Lab-on-chip' technology has been widely explored, giving greatly selective and sensitive results, saving time and money [1,2].

The sensors technology is manifesting in electrodes' surface modification by means of sensing platforms: (proteins, enzymes, nanomaterials, and macrocycles). The latter stated are principally divided into three major subtypes (Crown-ethers, cyclodextrins, and calixarenes/calixresorcinarenes). The resorcinarenes oligomers are well-known amphiphilic compounds resulting from cyclocondensation reactions between aldehydes and resorcinols. These oligomers' amphiphilic character (Hydrophobic and hydrophilic molecular parts) is the cause behind their encapsulation

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interactions (Host-Guest properties) with neutral molecules, cations, and anions, resulting in immense applications of calix-based sensors and extractants [2-4].

For HM detection motives, we report on the synthesis and characterization of novel resorcinarenes ionophores, their application as QCM sensing networks is also discussed. The results were satisfactory, and showed the macrocyclic capability to host the target toxic metallic elements. Furthermore, noble sensing characteristics were achieved.

2. EXPERIMENTAL

2.1 Synthesis and characterization

The C-dec-9-en-1-ylcalix[4]resorcinarene ***(Compound A)*** was synthesized and characterized as described formerly [5] . Both oligomers ***(Compounds B & C)*** were prepared from ***(Compound A)*** as starting reagent, and detailed chemically/ structurally characterized (FTIR, $^{1}H/^{13}C$ NMR, TG-DSC-MS, and P-XRD) in freshly published work [4].

2.2 QCM-I tests

New Au-quartz crystal chips were cleaned by means of acetone (10 min), Piranha solution ($1/3H_2O_2$+ $2/3\ H_2SO_4$) (10 min), rinsed with Milli-Q purity water, and dried. In order to immobilize the sensing platforms on the Au surface, resorcinarenes' solutions (2 mg/ml) were prepared using chloroform. Afterwards, volumes of 10 µl were drop-casted on sensor chips, and were dried at room temperature in a desiccator.

Milli-Q purity deionized water and analytical grade chemicals were used during all experiments. By diluting specific amounts of lead(II) nitrate ($Pb(NO_3)_2$) in deionized water, various concentrations of test solutions were prepared (5, 25, 250, 500, and 1000 ppm).

The detection tests were performed on a QCM-I instrument developed by (MicroVacuum Ltd. Hungary), The apparatus's resonance sensitivity in liquid is $2*10^{-1}$ Hz, the mass sensitivity is ≤ 1 ng/cm^2, and the dissipation sensitivity is $1*10^{-7}$. The Au-quartz crystals (AT-cut) had a 5 MHz fundamental resonance frequency, and a 14 mm diameter. A 40 µl volume flow-cell was used (200 µl/min flow-rate was maintained through peristaltic pump). Dissipation and resonance frequency variations were recorded for selected overtones/ frequencies (n = 1, 3, 5, 7 for 5, 15, 25, and 35 MHz). The detection measurements were PC-controlled via The BioSense Software V. 3.1

3. RESULTS & DISCUSSION

The synthesized ionophores' detection capability, coated onto QCM resonators, is explored against lead ions via *In-situ* QCM-I tests in aqueous solutions. An advanced parameter of layer characterization (Dissipation Energy) is also studied. Aiming to determine the best coating material in terms of frequency response, sensitivity, selectivity, and detection limits, various sensing characteristics are highlighted and compared.

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3.1 Frequency and dissipation shifts

Normalized frequency shifts in time, during the QCM sensors' exposure to Pb^{2+} aqueous solutions of concentrations up to 1000 ppm, are displayed in **Figure 1 (a, c)** for compounds B and C respectively. As predicted, the ΔFs decreased with increasing the HM amounts (concentration dependence). The responses were almost similar for low concentrations (5, 25, 250, and 500 ppm). Nevertheless, compound ***C*** reached an upper frequency value (ΔF = -23 Hz) at 1000 ppm compared to compound ***B*** (ΔF = -10 Hz), signifying more than two-folds difference.

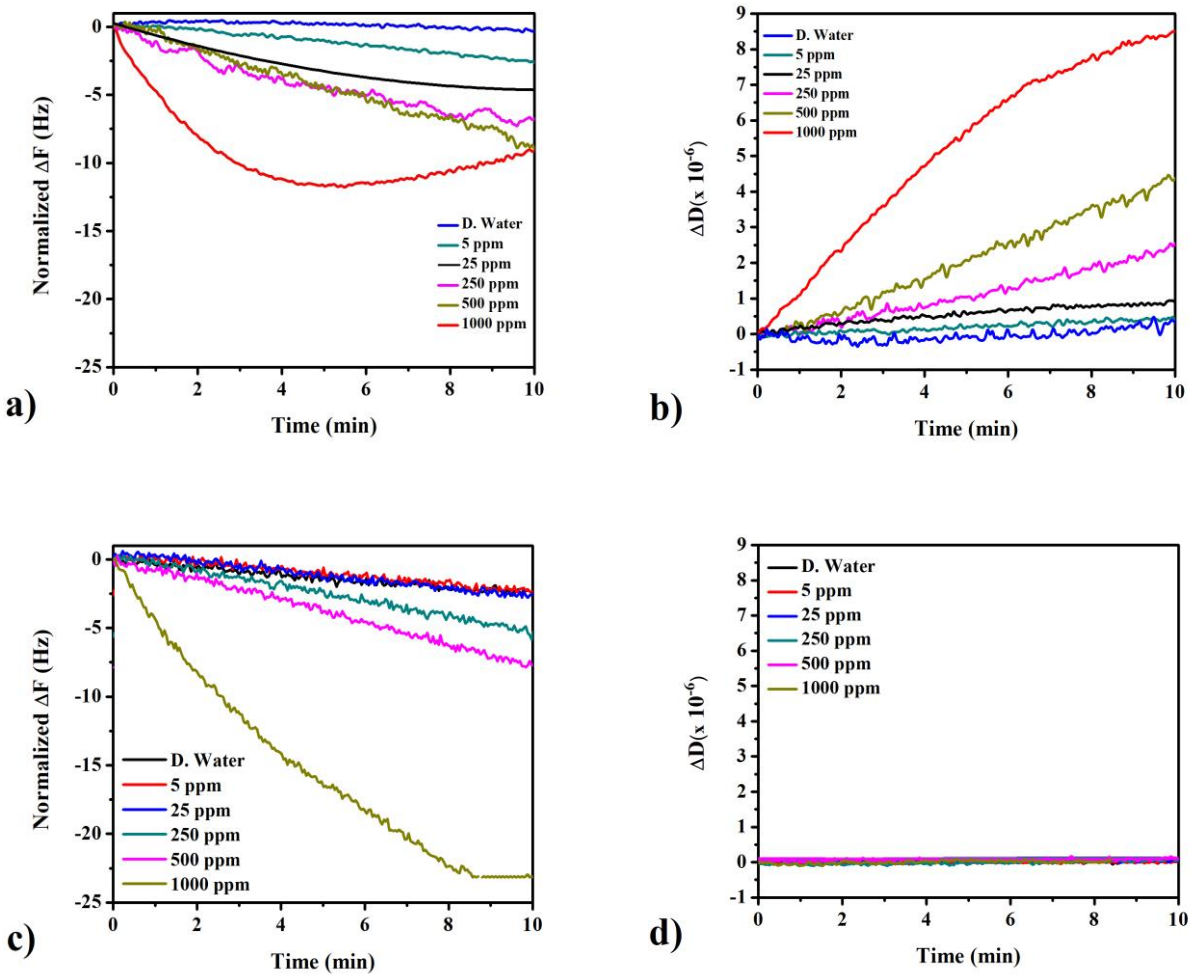

Figure 1: Frequency (a, c) and dissipation shifts (b, d) of compounds B and C based QCM sensors against various lead ions amounts in time

As a summary of ΔD_n and $\Delta f_n/n$ shifts. The collected data in **Table 1**, was registered from the end points of the shown curves in **Figure 1**. The damping or else energy loss values (ΔD) are good indicators of rigidity and softness (viscoelastic properties). Dissipation variations are providing truthful predictions regarding the Sauerbrey estimations' appropriateness, it's well-known that the upper limit of ΔD for treating a layer as rigid is about $2x10^{-6}$ [4]. Though, higher dissipation shifts ($\Delta D > 2x10^{-6}$) are indicative of the deposited film's softness, and alternative viscoelastic model must be applied to well describe both the binding mechanism, and the deposited layer's characteristics.

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Agreeing to the gotten dissipation shifts, the acquired data of compound ***C*** ($\Delta D_n < 2x10^{-6}$) indicated the macrocyclic network's rigidity, therefore, approving the Sauerbrey estimation's applicability. From another standpoint, compound ***B*** showed a significant viscoelasticity ($\Delta D_n > 2x10^{-6}$), especially at high Pb^{2+} (500, 1000 ppm) concentrations. However, a rigid character ($\Delta D_n \leq 2x10^{-6}$) was dominating for other concentrations, it may be explained by some loosely bound chains network, giving a soft coverage after the sensor's exposure to greater Pb^{2+} amounts ($C_{Pb^{2+}} > 250$ ppm).

Table 1: Dissipation energy and normalized frequency shifts of ionophores B and C at various Pb^{2+} concentrations (values are presented as average ± standard deviation)*

Measured value	**Concentrations (ppm)**	**Compound B***	**Compound C***
$\Delta F_n/n$ (Hz)	Blank (D. water)	- 0.30 ± 0.04	- 1.20 ± 0.10
	5	- 2.40 ± 0.30	- 2.50 ± 0.30
	25	- 4.80 ± 0.10	- 2.86 ± 0.04
	250	- 6.80 ± 0.40	- 5.72 ± 0.70
	500	- 8.50 ± 0.10	- 7.85 ± 0.40
	1000	- 10.00 ± 0.10	- 23.00 ± 0.01
ΔD_n (10^{-6})	Blank (D. water)	0.47 ± 0.23	0.10 ± 0.03
	5	0.54 ± 0.11	0.10 ± 0.01
	25	1.10 ± 0.34	0.21 ± 0.09
	250	2.50 ± 0.48	0.13 ± 0.01
	500	4.10 ± 0.23	0.11 ± 0.01
	1000	8.50 ± 0.07	0.10 ± 0.02

3.2 Possible detection mechanism

The HM detection mechanism is depending on the complexation (host-guest interaction), occurring between the ionophores' heteroatoms and the target toxic elements (charge transfer process). Afterwards, a HM accumulation is produced on the sensor's surface, the HM buildup can be detected piezo-gravimetrically. The potential formed complexes at the gold surface can be translated to reaction model equation 1, where M^{n+} stands for the lead ions and the ligand signifies ionophores B and C.

$$M^{n+}{}_{solution} + Ligand_{surface} \longrightarrow [M^{n+}\,Ligand_{surface}] \quad (1)$$

Both ionophores ***B*** and ***C*** showed frequency responses to all applied lead ions concentrations, supporting the functionality of the novel Pb^{2+} detection technique built on exploiting QCM-calix resonators.

3.3 Sensing characteristiques of ionophores B and C

Inferior detection limits (LOD) and admirable sensitivities is the utmost important aspect of detection. For both compounds (**B** and **C**), and in order to depict the sensing characteristics (sensitivities, detection limits, and linear ranges), **Figure 2** displays the calibration curves, whereas **table 2** shows the sensing characteristics.

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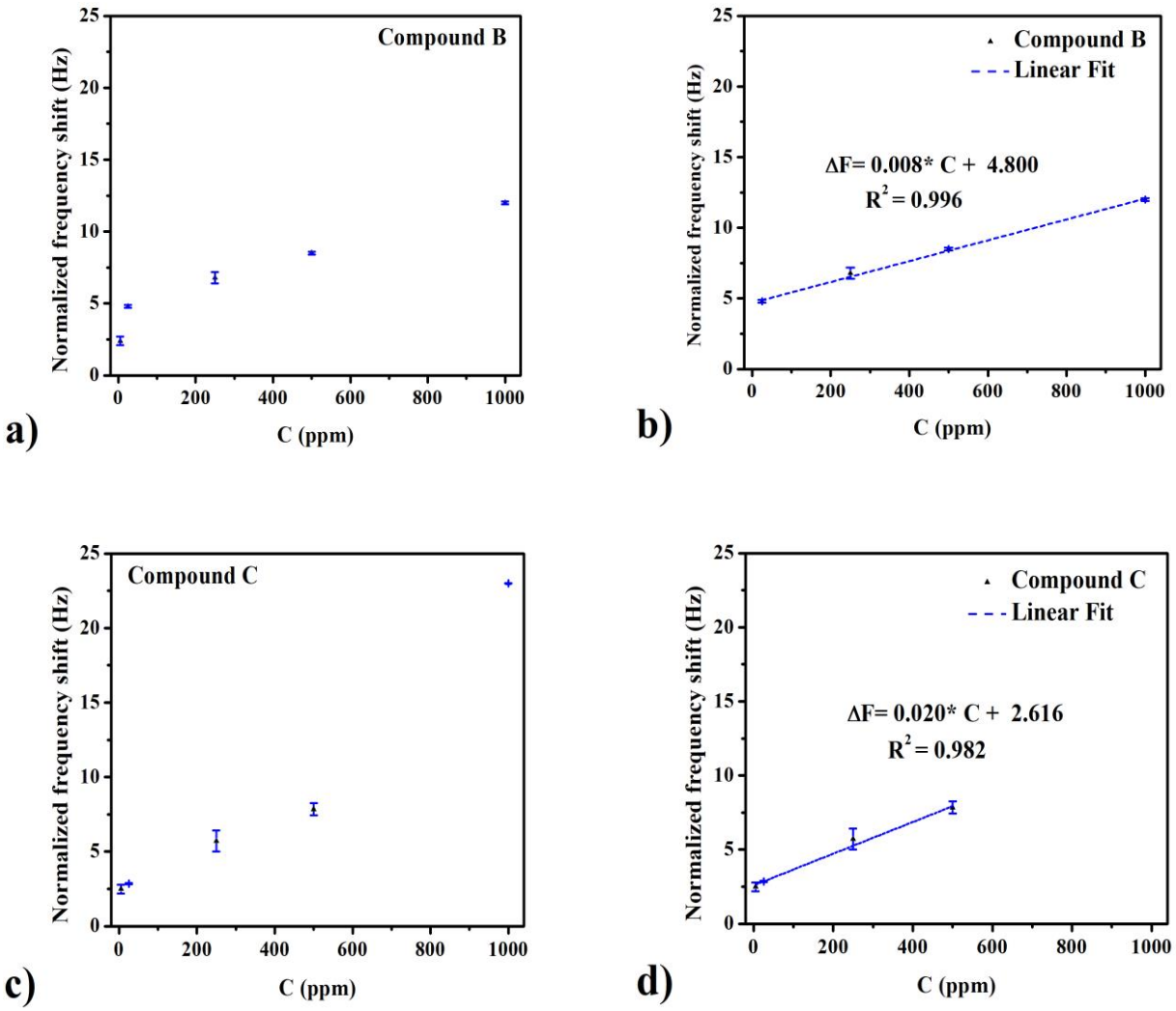

Figure 2: Calibration curves of the Calix-QCM based sensor in the Pb^{2+} concentration range of 5-1000 ppm for compound B (a) and compound C (c). Linear ranges based on calibration curves for compound B (b) and compound C (d).

Table 2: Sensing characteristics of ionophores B and C

Compounds	**Linear Range** ***(ppm)***	**Sensitivity** ***(Hz.ppm^{-1})***	**Limits of Detection** ***(ppm)***
B	25-1000	0.008	0.45
C	5-500	0.020	0.30

The LODs were calculated from the (3σ/S) relationship (Where 'S' stands for the linear regression's slope (Its representing the sensor's sensitivity as well), and 'σ' is the standard deviation of the fitted curve. The sensitivities were 0.008 and 0.020 Hz.ppm^{-1}, and the LODs were in the order of 0.45 and

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0.30 ppm for ionophores ***B*** and ***C*** successively, wide linear ranges were gotten for both cases as well. The obtained results confirm the superior selectivity and sensitivity of compound ***C*** to Pb^{2+} ions over compound ***B***, additionally, they approve the success of realization of Pb^{2+} detection prospect by means of Calix-QCM based chemosensors.

4. CONCLUSIONS

Novel enantiomeric calix[4]resorcinarenes bearing chiral moieties, namely: C-dec-9-enylcalix[4]resorcinarene-O-(S-)-α-methylbenzylamine ***(B)*** and C-dec-9-enylcalix[4]resorcinarene-O-(R+)-α-methylbenzylamine ***(C)***, were successfully synthesized and characterized via FTIR, ^{1}H NMR, ^{13}C NMR, TG-DSC-MS, and P-XRD.

Based on these ionophores, novel calix-QCM chemosensors were developed aiming to possibly detect lead ions in aqueous solutions at ppm or even ppb level. The QCM-I examinations proved that both sensing platforms showed noble linearities (***B***: R^2 = 0.996, ***C***: R^2 = 0.982), wide linear ranges (***B***: 25-1000 ppm, ***C***: 5-500 ppm), adequate sensitivities (***B***: 0.008 Hz.ppm^{-1}, ***C***: 0.02 Hz.ppm^{-1}), and LODs (***B***: 0.45 ppm, ***C***: 0.30 ppm). ***Ionophore C*** showed advantages over ***ionophore B*** in terms of sensitivity and selectivity toward lead ions.

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